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The Dissociation Pressures and the Ignition of Magnesium Ammonium Phosphate Hexahydrate

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DISSERTATION

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THE DISSOCIATION PRESSURES AND THE IGNITION OF MAGNESIUM AMMONIUM PHOSPHATE HEXAHYDRATE

In 1847 Heintz[1] published a method for the determination of magnesium or phosphorus based on the precipitation of these elements as magnesium ammonium phosphate hexahydrate, and the ignition of this precipitate to magnesium pyrophosphate. This method, as improved by Gibbs[2] in 1873, has come into very general use. It, however, was and is subject to a large number of possible errors, and there have, therefore, appeared in the last sixty years, ninety or more research reports upon its various phases.

The facts brought out by these studies fall mainly into two groups: those dealing with the conditions necessary for the quantitative precipitation of the magnesium or phosphorus in the form of pure $MgNH_4PO_4 \cdot 6H_2O$ and those dealing with the ignition of this precipitate to $Mg_2P_2O_7$. The subject has been attacked from almost every conceivable angle. But it seems noteworthy that, although the salt precipitated is a hydrate which loses its water of hydration during the ignition process, there should be no information whatever on the dissociation pressures of the compound. Furthermore, it is a hydrated ammonium salt which loses both its water of hydration and its ammonia, and an orthophosphate which is converted to a pyrophosphate by the loss of water of constitution.

It seemed probable, therefore, that a study of magnesium ammonium phosphate from the viewpoint of the phase rule might yield valuable information. According to the phase rule, a salt-hydrate that dissociates into a lower hydrate or anhydrous salt and a gaseous phase is a two-component system, and with three phases present it is uni-variant. A large number of such systems have been studied and reported in the literature by a number of reliable investigators. Among those who have done much to improve the method for measuring dissociation pressures of such systems are: Johnston[3], whose excellent apparatus and method present a real improvement; Baxter and Lansing[4]; Frowein[5]; Menzies[6]; and

Wilson[7]. The last two mentioned give good criticisms of the many preceding researches and list the errors often made in manipulation and measurement. We have endeavored in the present research to reduce the effect of as many of these errors as possible.

The studies referred to above deal with two-component, three phase, uni-variant systems. Magnesium ammonium phosphate hexahydrate also forms such a system when it dissociates into a lower hydrate and water. However, in this case there is a further dissociation yielding a magnesium acid phosphate and ammonia, thus forming a third component and a third solid phase. The ammonia, however, does not form an additional phase, as there can be only one vapor phase and water vapor is already present. This system, consisting of three components present in four phases, is also uni-variant and has, therefore, a definite dissociation pressure at any fixed temperature. Both the two-component and the three-component systems are represented in this research. Systems 1, 4, and 5 listed below consist of two components, while systems 2 and 3 contain three components. The following systems were studied:

System 1. $MgNH_4PO_4.6H_2O \rightleftharpoons MgNH_4PO_4.H_2O + H_2O$.
System 2. $MgNH_4PO_4.6H_2O \rightleftharpoons MgNH_4PO_4.H_2O + MgHPO_4.3H_2O + H_2O + NH_3$.
System 3. $MgNH_4PO_4.H_2O \rightleftharpoons MgNH_4PO_4 + Mg_2P_2O_7 + NH_3 + H_2O$.
System 4. $MgHPO_4.7H_2O \rightleftharpoons MgHPO_4.3H_2O + H_2O$.
System 5. $MgHPO_4.3H_2O \rightleftharpoons MgHPO_4.H_2O + H_2O$.

Preparation and Analysis of Materials

$MgNH_4PO_4.6H_2O$. Equivalents of $Na_2HPO_4.12H_2O$, carefully purified, and magnesia mixture, (usually about one liter of each, of one-tenth molar concentration), were poured together and the precipitate dissolved with HCl. Then very dilute ammonium hydroxide was added slowly with constant stirring until the salt was almost all precipitated. Then more concentrated ammonium hydroxide was added until its concentration was about one molar. After standing for four hours or more, it was washed with water until a sample of it dissolved in one-tenth molar nitric acid gave no test for chloride with silver nitrate. It was then filtered on a hardened filter paper in a Buchner funnel, washed with four 50 cc. portions of absolute ethyl alcohol, then with four 50 cc. portions of anhydrous ether; it was then transferred to a bottle and suction applied by means of an oil pump for an hour. The salt adhering to the filter paper was rejected to reduce the danger of organic impurities. By this method a number of lots were prepared, all of which were shown by the microscope to be distinctly and uniformly crystalline, gave the theoretical loss in weight on ignition closer than one part per thousand, (Table I) gave the theoretical percentage of ammonia within about one part per thousand, and gave snow-white residues on ignition under all conditions.

$MgNH_4PO_4.H_2O$. This salt was prepared by the same method as the hexahydrate except that it was precipitated from boiling solution, kept in an oven in the mother liquid at 100°-102° for 24 hours, washed with boiling water, and dried in an oven at 106° for eight hours. It was very uniformly crystalline, consisting of square, flat crystals, gave the theoretical loss in weight upon ignition, the theoretical ammonia content, and gave snow-white residues upon ignition.

$MgHPO_4.7H_2O$. Equivalents of $MgSO_4.7H_2O$ and $Na_2HPO_4.12H_2O$ in solutions were mixed; the precipitate was dissolved by adding a small amount of sulfuric acid, and re-precipitation was effected by adding dilute sodium hydroxide solution. The precipitate was washed with water, alcohol, and ether, dried on a glass plate until free from ether, and bottled. It consisted of large needle-shaped crystals, and gave the theoretical loss of weight upon ignition.

$MgHPO_4.3H_2O$. When the $MgHPO_4.7H_2O$ still in its mother liquid was warmed to 35° the long needle-like crystals changed to the rhombic form. Upon ignition these gave the theoretical loss in weight for the reaction:

$$2MgHPO_4.3H_2O \rightarrow Mg_2P_2O_7 + 7H_2O\,.$$

A summary of the data on the analysis of the above salts is given in Table I.

TABLE I

Analysis of Materials

Salt	*Residue on Ignition*				*Ammonia Content*			
	Weight of salt g.	Residue g.	Experi-mental % residue	Theoretical % residue	Weight of salt g.	cc. of 0.09407 N acid required	Experi-mental % ammonia	Theoretical % ammonia
$MgNH_4PO_4.6H_2O$	0.8007	0.3630	45.34	45.36	1.5002	64.78	6.920	6.938
	0.9786	0.4435	45.32		1.0336	40.70	6.929	
	1.0911	0.4948	45.35		1.1021	47.64	6.926	
$MgNH_4PO_4.H_2O$	0.9920	0.7088	71.45	71.65	0.9215	62.04	10.96	10.96
	0.8262	0.5904	71.46		0.6257	41.67	10.67	
	1.4465	1.0336	71.48		0.4773	31.74	10.66	
$MgHPO_4.3H_2O$	0.9238	0.5864	63.48	63.84				
	0.9226	0.5850	63.41					
	1.0433	0.6626	63.51					
$MgHPO_4.7H_2O$	0.7904	0.3567	45.13	45.18				
	1.1157	0.5035	45.13					
	0.9069	0.4087	45.07					

Apparatus

The apparatus used for the measurement of pressures is a modification of that of Kiehl and Wallace[8]. Some of the systems, in fact, may well be measured with practically the same set-up. But the first salt studied, $MgNH_4PO_4.6H_2O$, developed such exceptionally high dissociation pressures that with this form of apparatus it was impossible to prevent the condensation of the water. The water vapor pressure produced was so near that of water itself that even a slight difference of temperature betwen the furnace and the steam-jacket caused condensation in the cooler portion of the container.

A modification was, therefore, made, whereby this condensation was prevented, the set-up was simplified, and manipulation was made much easier. The essentials of the set-up are shown in Fig. I (a). The usual furnace and steam-jacket were combined into a unit consisting almost entirely of pyrex and a resistance wire. A double walled cylinder, C, with a vacuum between the walls, of heavy pyrex glass, 27 centimeters long and 6.5 centimeters inside diameter was used as a chamber for the heater. The ends were closed with corks covered with heavy asbestos paper. The heating unit, H, consisted of a smaller pyrex cylinder upon which was wound 27 feet of 28-gauge nicrome wire. When this heater was connected with the 110 volt circuit, with the proper resistance in series any temperature from room temperature up to 425° could be secured.

The manometer, M, made of 7 millimeter (inside diameter) pyrex tubing, was three meters long, and could be used for measuring pressures up to five and one-half atmospheres. It was mounted on a steel beam which had attached to it an invar bar, I, containing a silver millimeter scale, and a heavy steel bar upon which the hair-lined reading glass, S, moved. The outlet, P, was connected to an oil-pump, by which a vacuum of 0.2 mm. pressure could be secured. When pressures less than one atmosphere were to be measured an air valve at O was used to admit air to counter-balance the pressures developed by the system; and for pressures greater than an atmosphere, O was connected to a high-pressure hydrogen cylinder by means of heavy walled rubber tubing which was wrapped tightly with tire-tape. The connection, R, was also wrapped pressure tubing, and permitted tilting the furnace after evacuation. Before being wrapped the rubber tubing was thoroughly massaged several times, inside and out, with warm castor-oil, to make it less pervious to gases. This oiled and wrapped pressure tubing retained pressures of five and one-half atmospheres with perfect satisfaction.

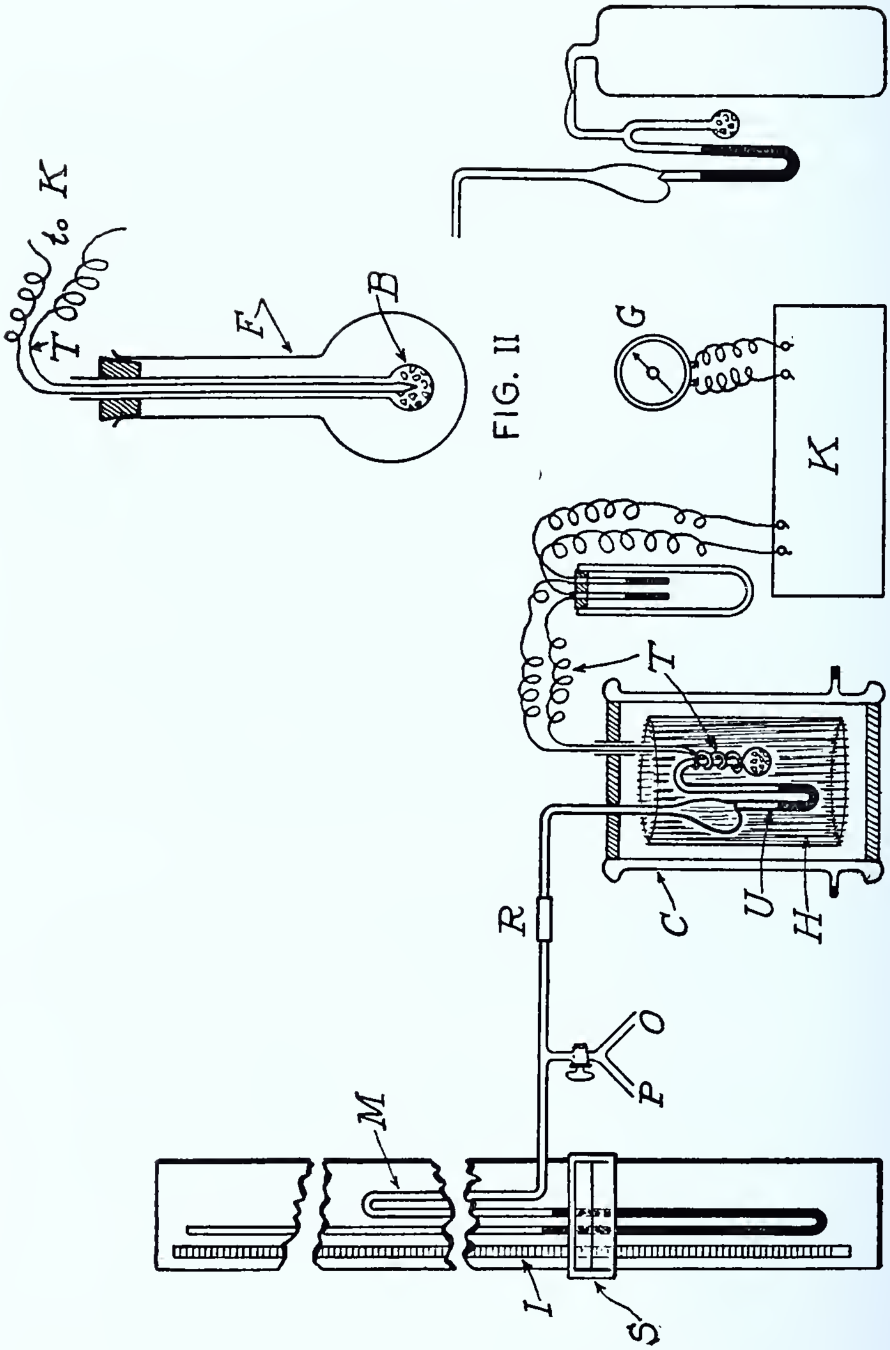

FIGURE I-A. Apparatus used for measurement of dissociation pressures.
FIGURE I-B. Modified manometer used in determining ratio of water to ammonia.
FIGURE II. Apparatus used for determining temperature of "flash."

As a confining liquid for the gases formed by the dissociation mercury is usually the best because it is the least likely to absorb the gases present. In this research mercury was found excellent for those systems where the temperatures used were low. But the kind of systems measured, and the method and apparatus used required the confining liquid be kept at the same temperature as the salt itself. Since mercury boils at 357° a large correction due to the vapor pressure of mercury itself would be required as the temperature approached this point. Above this temperature it will boil and distill out of the capillary into the cooler portion of the it will boil and distill out of the capillary into the cooler portion of the tube. In looking for a confining liquid that did not have this limitation in this temperature region, Wood's metal was found, and proved to be excellently suited. It has practically no vapor pressure at the temperatures used. When a sample of the purest material obtainable was placed alone in the dissociation pressure apparatus no appreciable pressure developed at even the highest temperature used for measuring dissociation pressures. When the temperature was increased to 300° C a pressure of 5 millimeters was developed.

To aid in levelling the confining liquid in the differential manometer a chromium-plated strip of brass three-quarter inches wide by three inches long with a millimeter scale engraved upon it was fastened to the legs of the manometer.

For reading temperatures up to 350° C a copper-constantan thermocouple was used, and above that temperature a platinum platinum-rhodium thermocouple. The electromotive force was measured by means of a type K Leeds and Northrup potentiometer, a Leeds and Northrup Model 4 Standard Weston Cell, and a water-and-ice cold junction. The thermocouples were standardized against the melting points of samples of tin, lead, zinc, and aluminum from the United States Bureau of Standards, the boiling points of water, alcohol, and ether, and the freezing point of water.

For determining the temperature of luminescence of the salts the following apparatus, as shown in Fig. II was used. F is a long-necked, round-bottomed, 100 cc. pyrex flask which served as an air bath. B was a bulb of about 15 millimeters inside diameter, on a pyrex tube of about 7 millimeters inside diameter. The bulb held from 0.1 to 0.2 g when about half filled. T, the platinum platinum-rhodium thermocouple had its junction in the middle of the salt.

For heating the salts in vacuum, a thick-walled pyrex tube 40 centimeters in length and 5 centimeters in diameter, with a ground-glass cap which was fitted with a stop-cock, was used. The lower third was placed in an electric furnace and the upper part protected from the heat of the furnace by two tightly fitting asbestos sheets, so that when evacuated the lower part could be heated to above 450° while the upper end remained at the room temperature. A platinum crucible containing the salt was lowered into the tube by means of a glass rod bent at the bottom into the form of a ring.

For the ignitions, the results of which are recorded in tables X and XI, porcelain Gooch crucibles were used, and the ignitions were made over Meeker burners or in a muffle-furnace capable of maintaining a temperature of 1100° C.

Method

Dissociation Pressures. The much used static method for measuring dissociation pressures of salt hydrates was employed. When pressures were to be read, the bulb, filled with a sufficiently large sample of the salt (0.1 to 0.25 g) was sealed to the small manometer. When mercury was used as a confining liquid it was poured into the reservoir, and the manometer connected at R. The system was then evacuated and left overnight. The next morning the system was again evacuated and the mercury tilted into the capillary. Then the heat was turned on and the desired temperature maintained till the pressure became constant. When Wood's metal was used the procedure was exactly the same except that the system was heated to 75-100° before the liquid was tilted in. When constant pressure was reached the temperature was increased and the new equilibrium-pressure found. When the highest pressure to be measured had been determined, the process was reversed; that is, the temperature was reduced step-wise, and the pressure found for each temperature. The temperature pressure curve was considerd a true equilibrium curve only when the curve for increasing temperatures coincided with that for decreasing temperatures. The same equilibrium pressure was obtained when approached from either lower or higher temperatures.

The entire experiment was then repeated, using a mixture of the salt being studied and an equivalent weight of the solid phase believed to have formed. When the curve thus obtained was the same as for the original salt alone the identity of the solid phase was established and the equilibrium curve confirmed.

Evidence for Phases Present

Since no distinctive tests are known by which the hydrates of $MgNH_4PO_4$ and of $MgHPO_4$ may be identified when in the presence of each other, it is necessary to establish the presence of all phases by reasoning from the results obtained. The evidence showing which substances are formed by the dissociation in each system is given below.

System 1. $MgNH_4PO_4.6H_2O \rightleftharpoons MgNH_4PO_4.H_2O + H_2O$

1. The hexahydrate forms monohydrate because the two when mixed give the same curve as the hexahydrate alone.

2. The monohydrate is formed from the hexahydrate and can be isolated in fairly pure form if the gas evolved at 50° or less is removed as fast as formed.

3. Red litmus in the reaction chamber does not change to blue below 50°, nor does it change when moistened and exposed to the gas which has been removed from the reaction chamber. Ammonia is not given off below 50°.

System 2. $MgNH_4PO_4.6H_2O \rightleftharpoons MgNH_4PO_4.H_2O + MgHPO_4.3H_2O + H_2O + NH_3$

1. A mixture of the first and second, or first, second, and third solid phases gives the same curve as the first alone.

2. The monohydrate is formed from the hexahydrate and can be isolated in fairly pure form if the gas evolved at 50° is removed as fast as formed.

3. $MgNH_4PO_4.H_2O$, when heated in a closed system under the high vapor pressure of water furnished by the hexahydrate, first loses ammonia, forming $MgHPO_4.H_2O$. (See System 3.) But under the conditions prevailing here, the monohydrate is converted to the trihydrate, because the trihydrate is the salt in whose range of existence the pressure-temperature curve for System 2 lies.

4. The water and ammonia, on cooling, form a solution which quickly turns red litmus blue, and smells strongly of ammonia.

System 3. $MgNH_4PO_4.H_2O \rightleftharpoons MgNH_4PO_4 + Mg_2P_2O_7 + NH_3 + H_2O$

1. Zinc acetate reagent or silver nitrate gives tests for pyrophosphate whenever both ammonia and water are found in the gaseous phase.

2. Mixtures of the first and second, or first, second and third phases give the same pressure-temperature curve as the first alone.

3. When $MgNH_4PO_4.H_2O$ is heated in an open vessel so as to drive off a part of the volatile matter, it always retains a larger percentage of its NH_3 than of its H_2O, as shown below:

Temp. to which heated	% NH_3 retained	% H_2O retained
340° C.	24.5	17.5
335° C.	29.5	24.0
350° C.	17.0	12.0
580° C.	6.0	2.0

This shows that the water of hydration is given off before the NH_3.

4. When $MgNH_4PO_4.H_2O$ is heated in the temperature-pressure apparatus, and the gaseous phase *at equilibrium* is analyzed, the ratio of water to ammonia is found to be about 3:1, as shown under "Results." This shows that some of the substance which has lost water has not lost ammonia, for each molecule of $MgNH_4PO_4.H_2O$ contains only one molecule of water of hydration for every molecule of ammonia.

5. Since the system at equilibrium always gives positive tests for pyrophosphate whenever ammonia is present, the $MgNH_4PO_4.H_2O$ must lose both NH_3 and H_2O to form $Mg_2P_2O_7$ without the existence, *at equlibrium,* of any other solid phase; for a uni-variant three-component system can have only four phases.

System 4. $MgHPO_4.7H_2O \rightleftharpoons MgHPO_4.3H_2O + H_2O$

1. Either the heptahydrate or a mixture of the two hydrates gives the same curve.

2. If the vapors formed are pumped off, it is found that there is a great decrease in pressure at equilibrium when the composition of the resulting solid is approximately $MgHPO_4.3H_2O$.

3. Crystals appear which have the same form as those of pure $MgHPO_4.3H_2O$.

System 5. $MgHPO_4.3H_2O \rightleftharpoons MgHPO_4.H_2O + H_2O$

1. Zinc acetate reagent does not give a test for pyrophosphate even when a great pressure has been developed. (This reagent, consisting of a thirty-two hundredths molar zinc acetate solution in the presence of one-eighth its volume of glacial acetic acid, has been shown by Kiehl and Coats[9] to be sufficiently sensitive to detect 0.0006 molar pyrophosphate in the presence of 0.1 molar ortho-phosphate and 0.1 molar monometaphosphate.)

2. If the vapors formed are pumped off, it is found that there is a great decrease in equilibrium pressure when the composition of the resulting solid is approximately $MgHPO_4.H_2O$.

Determining the Ratio of Water to Ammonia

To determine the ratio of water to ammonia in System 3 where both of these substances are liberated as gases, the following method was used: A receptacle resembling a large test tube was sealed to the bulb containing the salt as shown in Fig. 1 (b). There was a constriction in the tube which connected the bulb to the remainder of the apparatus to facilitate sealing off the bulb when equilibrium was established. In addition to the regular stopper in the top of the furnace, an extra asbestos stopper was used immediately beneath it, having a small hole just over the constriction in the tube.

The apparatus was set up in the usual way except that the salt bulb contained about a gram of salt instead of the usual 0.2 to 0.3 g charge. When equilibrium was established the temperature was noted, the upper stopper removed, and the large bulb quickly sealed off with a small, hot flame. This could be done with practically no change in temperature, and the levelling liquid show no change in position. The bulb was then inserted into a measured volume of 0.02N H_2SO_4 and the tip broken off. The excess acid was back-titrated with 0.02N NaOH and the standard volume of the ammonia as a gas was calculated. The standard volume of all the gases present was also calculated and the water determined by difference.

The method worked nicely up to a total pressure of one atmosphere.

Test Ignitions

For making the test ignitions, the results of which are listed in Tables X and XI, the following method was used: A stock solution was made by placing $MgNH_4PO_4.6H_2O$ in distilled water and dissolving it by adding dilute hydrochloric acid. The concentration was such that 45 cc. of the solution yielded approximately 0.15 grams of magnesium pyrophosphate. Of this solution 45 cc. was measured by a burette into a 250 cc. beaker, 50 cc. of water and six drops of magnesia mixture were added, and precipitation effected by adding very dilute ammonium hydroxide at 90-100°. After eight hours or more the precipitate was transferred to a Gooch crucible and dried in an oven at 110°. Two methods of ignition were used. In the first the precipitates were heated over a low Bunsen flame for ten minutes and then over the hottest flame obtainable with a Meeker burner for an hour, with additional periods of fifteen minutes until constant weight was reached. In the second method the precipitates were heated in a muffle-furnace at 480° until constant weight was reached, and then ignited in a very hot Meeker flame until luminescence occurred.

Results

The temperature-pressure data for four runs on System 1 are given in Table II. All pressures are recorded in millimeters of mercury at 0° C.

TABLE II

Experimental Data for Systems 1 and 2

System 1. $MgNH_4PO_4.6H_2O \rightleftharpoons MgNH_4PO_4.H_2O + H_2O$ (Below 60°).
System 2. $MgNH_4PO_4.6H_2O \rightleftharpoons MgNH_4PO_4.H_2O + MgHPO_4.3H_2O + NH_3 + H_2O$ (Above 60°).

Run No.: 1.		2.		3.		4.	
T.° C.	P. mm.	T.	P.	T.	P.	T.	P.
41.1	34.2	39.0	32.1	40.0	35.0	42.3	34.9
50.0	71.1	51.9	83.0	51.6	77.0	55.5	79.9
53.5	78.2	59.0	100.0	55.4	89.3	57.0	88.9
62.0	122.5	59.9	113.0	59.0	106.3	61.5	117.5
65.0	144.8	63.6	133.4	61.5	121.4	66.0	139.5
73.0	205.1	65.0	154.8	62.8	126.7	77.1	275.4
85.0	377.9	71.2	196.2	68.1	162.1	86.0	390.6
87.0	407.9	75.0	242.2	69.2	169.9	102.5	710.1
89.5	450.7	88.3	450.8	74.0	220.0	118.9	1208.1
94.0	513.0	100.1	670.1	81.9	292.2	119.6	1240.8
108.0	846.8	106.2	823.0	88.5	373.4	132.0	1809.8
112.5	957.0	115.2	1020.0	89.6	423.2	133.6	1941.5
125.6	1423.0	125.6	1448.8	102.2	704.6	135.1	2008.0
128.5	1620.0	137.0	2113.3	103.4	713.9	139.6	2264.1
131.0	1734	140.5	2271.7	111.9	948.8	146.0	2536.0
132.5	1838	146.2	2655.0	112.6	952.6	152.8	3273.3
134.8	1926	152.4	3263.3	118.0	1151.1		
136.5	1950	156.2	3696.7	120.0	1238.7		
150.0	2846			120.5	1278.9		
152.8	3423			134.4	1969.9		
				140.5	2352.0		
				142.6	2385		
				159.1	3835		

In order to select from the temperature-pressure data recorded above, those values which would as nearly as possible represent the true values, the following method was used: From the data for each of the four runs a curve was drawn; from these curves the pressure values for a particular temperature were read and averaged. From these average values the final curve for the system was drawn.

Below sixty degrees no ammonia is noticeable in the gaseous phase. The system is univariant and may be expressed by two components. Above sixty degrees, moreover, the ammonium salt has reached an appreciable dissociation which produces another phase while the system still has one degree of freedom. Three components are necessary, therefore, to express it. Data in Table II and the curve in Figure III are the combined results of the systems studied as systems 1 and 2. There are consequently two effects—the dissociation of the hexahydrate and the dissociation of the ammonium salt—one superimposed gradually upon the other.

Thus the four curves constructed from the data in Table II give the following readings:

Pressures at 10° Intervals for Systems 1 and 2

Run No.	1.	2.	3.	4.	Ave.
40°	33.2	32.4	35.0	32.9	33.4
50°	71.1	67.3	75.2	65.5	69.8
60°	108.4	110.7	110.9	106.0	109.0
70°	177.0	180.3	177.5	177.1	177.5
80°	298.6	308.4	295.1	307.1	302.3
90°	448.3	456.4	440.1	455.1	450.0
100°	650.2	666.5	645.4	665.4	651.9
110°	884.3	916.8	886.1	918.8	901.5
120°	1226	1244	1228	1268	1242
130°	1678	1684	1688	1700	1688
140°	2220	2295	2300	2290	2266
150°	2860	3000	2899	2961	2935
155°	3560	3540	3460	3520	3521
159.1			3834		3834

The temperature-pressure curve for the system was drawn from these average values in Table III, and is shown in Figure III.

The other systems studied were dealt with in the same manner, and the results recorded in the following pages.

TABLE IV

Experimental Data for System 3

$MgNH_4PO_4.H_2O \rightleftharpoons MgNH_4PO_4 + Mg_2P_2O_7 + H_2O + NH_3$

Run No.: 1.		2.		3.		4.	
T° C.	P. mm.	T.	P.	T.	P.	T.	P.
121.9	9.0	131.7	11.1	127.8	9.8	125.0	9.5
131.0	11.1	145.5	18.9	131.9	12.2	132.7	14.7
165.0	52.8	152.8	24.9	137.4	13.9	138.0	17.5
209.8	217.4	159.9	35.0	149.1	22.5	163.8	45.3
227.5	353.3	183.6	87.4	164.8	43.9	175.1	64.8
246.5	684.9	198.7	141.0	175.7	62.8	186.6	90.8
253.3	908.5	227.0	311.8	188.4	97.2	195.1	136.2
261.6	1280.0	250.2	735.4	199.2	143.8	203.0	174.5
270.8	1888.0	265.0	1389.0	210.7	207.7	215.5	235.8
279.9	2873.4	270.0	1839.6	231.0	369.1	230.9	392.0
280.9	3187.4	274.9	2400.0	250.0	767.5	258.9	1145.0
281.9	3429.4	279.1	2929	254.8	1117.0	272.8	2209.0
				274.0	2514.2	279.5	3089.0
				281.6	3327.2		

TABLE III

TABLE V

Pressures at 10° Intervals for System 3

Run No.	1.	2.	3.	4.	Ave.
130°	10.6	10.6	10.8	12.9	11.2
140°	15.9	15.5	15.6	17.9	16.2
150°	26.0	22.0	23.1	25.9	24.3
160°	41.2	35.0	34.8	38.7	36.9
170°	61.0	54.1	51.7	57.0	55.9
180°	82.5	76.1	73.4	81.8	78.5
190°	112.0	106.9	104.6	111.9	111.4
200°	155.2	146.9	143.2	153.5	149.6
210°	209.8	198.6	194.0	207.9	202.5
220°	286.8	266.2	262.5	281.4	276.9
230°	388.8	365.9	389.8	382.0	376.1
240°	540.4	517.0	525.8	539.4	530.7
250°	770.0	750.5	770.5	772.5	765.9
260°	1210	1176	1180	1195	1191
270°	1870	1840	1898	1187	1874
280°	3105	3110	3157	3145	3129

TABLE VI

Experimental Data for System 5

$MgHPO_4.3H_2O \rightleftharpoons MgHPO_4.H_2O + H_2O$

Run No.: 1.		2.		3.		4.	
T.° C.	P. mm.	T.	P.	T.	P.	T.	P.
33.0	10.5	51.0	26.2	44.0	17.5	27.0	10.0
41.0	13.0	54.0	31.5	49.9	25.8	32.0	12.2
49.0	21.1	62.0	43.5	51.0	27.1	42.0	14.7
59.5	32.2	76.1	72.2	55.0	32.5	51.0	25.1
70.0	53.5	88.0	116.6	61.4	42.0	61.5	36.0
87.7	106.6	102.6	168.2	69.0	61.0	78.0	71.5
94.6	133.5	114.3	243.6	76.6	80.0	87.0	109.8
106.0	195.0	131.8	384.6	81.0	85.2	105.0	199.1
110.8	227.7	135.0	410.7	88.0	116.6	114.0	251.0
119.0	282.4	145.0	502.6	110.0	218.4	131.9	389.6
130.0	372.2	150.8	604.0	111.4	240.9	135.0	413.6
143.1	514.2	155.5	684.0	133.0	404.4	157.0	696.1
151.2	602.2	158.5	1300	156.0	691.0	159.0	1470
154.5	697.6						
159.0	1500						

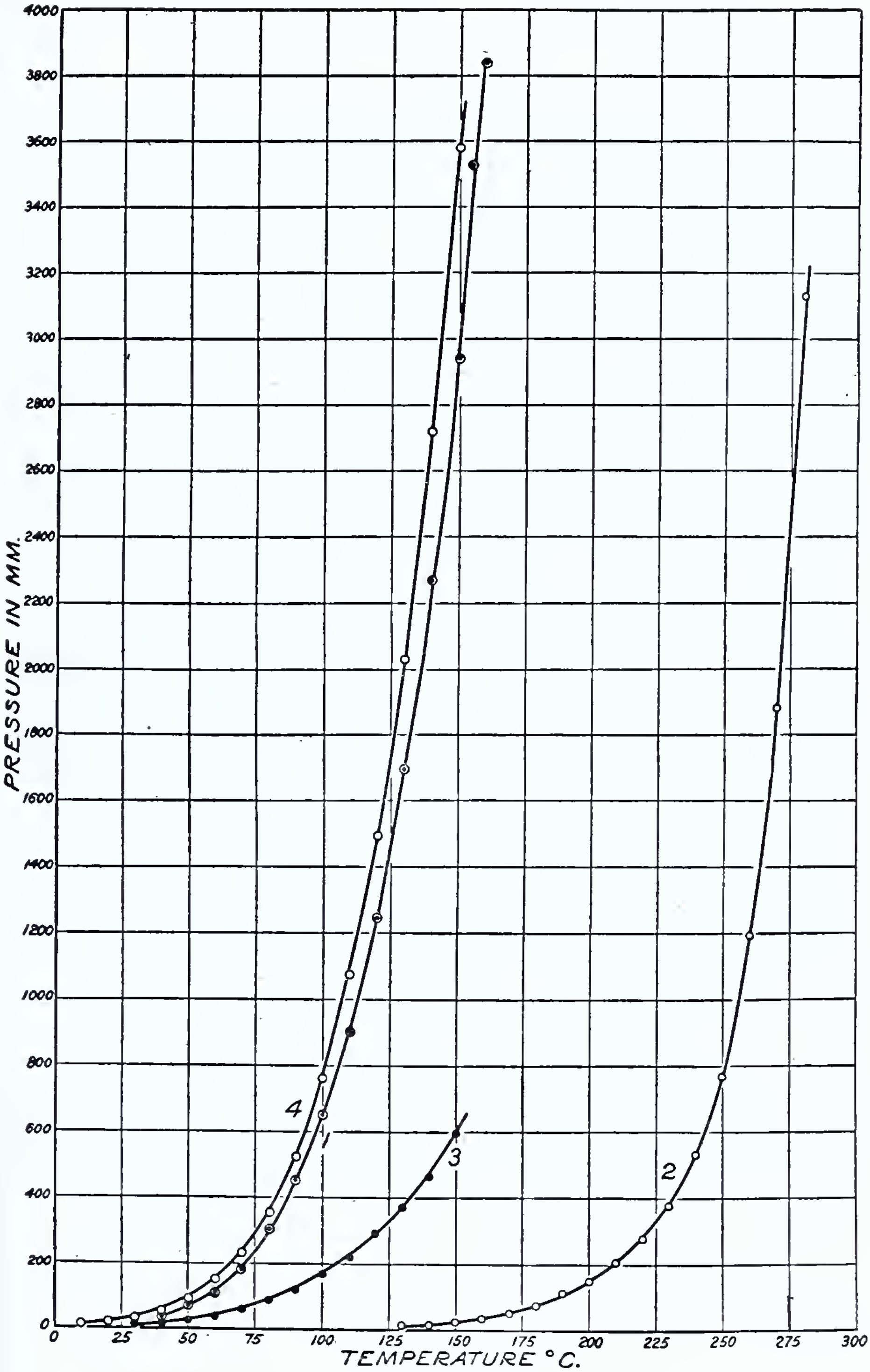

FIGURE III

The Dissociation Pressure Curves for the Systems:

Curve 1. $\left\{ \begin{array}{l} MgNH_4PO_4.6H_2O \rightleftharpoons MgNH_4PO_4.H_2O + H_2O \text{ (Below 60°).} \\ MgNH_4PO_4.6H_2O \rightleftharpoons MgNH_4PO_4.H_2O + MgHPO_4.3H_2O + H_2O + NH_3 \end{array} \right.$
(Above 60°).

Curve 2. $MgNH_4PO_4.H_2O \rightleftharpoons MgNH_4PO_4 + Mg_2P_2O_7 + NH_3 + H_2O$.

Curve 3. $MgHPO_4.3H_2O \rightleftharpoons MgHPO_4.H_2O + H_2O$.

And the vapor pressure curve for the system:

Curve 4. Liquid water ⇌ water-vapor.

TABLE VII

Pressures at 10° Intervals for System 5

Run No.	1.	2.	3.	4.	Ave.
30°	9.6	10.4	10.8	10.2	9.9
40°	12.8	14.8	15.0	13.9	14.1
50°	21.9	25.3	25.3	24.6	24.3
60°	33.0	40.5	40.5	35.1	37.3
70°	53.0	60.0	61.0	54.6	59.7
80°	83.8	86.1	87.8	82.8	85.0
90°	118.5	119.1	122.7	120.0	120.2
100°	166.5	162.0	167.5	166.0	165.4
110°	222.5	216.8	220.2	225.9	221.4
120°	291.0	284.8	290.0	291.5	289.6
130°	372.2	368.1	372.0	371.8	371.2
140°	467.5	464.0	468.0	469.5	467.2
150°	589.0	590.5	598.0	590.0	591.9
155°	664.0	674.0	674.2	663.8	669.0

In System 5 the reaction is quickly and completely reversible up to about 157°, and the system consists simply of the two hydrates in equilibrium with water-vapor. Above 157° the pressure increases in a very rapid and irregular way, and the reaction is not feasibly reversible. Pure $MgHPO_4.3H_2O$ which has been heated in the reaction vessel to 158° or more gives a positive test for pyro-phosphate with zinc acetate reagent, while that kept below this temperature shows no trace of it.

In System 3 the reaction is completely reversible, although extremely slow. Pyrophosphate appears at a very low temperature, at 200° or less. Here the pyrophosphate seems to convert back to orthophosphate much more readily than in a similar situation in System 5.

Determining the Ratio of Water to Ammonia

The ratio of water to ammonia in the vapor phase at equilibrium for System 3 was determined at those temperatures at which the dissociation pressures were approximately one atmosphere and one-half an atmosphere. The analysis of the mixtures at these pressures gave the following data:

TABLE VIII

The Ratio of Water to Ammonia in the vapor phase of System 3 at equilibrium

	Volume of gas collected	Temperature	Total Pressure collected	Standard volume of gas	Standard volume of NH_3 by titration	% Ammonia by volume	% Water by Volume
1.	52 cc	246.°	726.0	28.24	7.82 cc	27.71	72.29
2.	52 cc	245.°	695.8	26.11	6.77	25.95	74.05
3.	52 cc	245.°	703.6	25.62	6.65	25.97	74.03
					ave.:	26.54	73.46
4.	52 cc	229 °	347.1	12.91	3.45	26.71	73.29
5.	52 cc	229 °	340.9	12.26	3.31	26.59	73.41
6.	50 cc	230 °	340.0	12.17	3.27	26.85	73.15
					ave.:	26.72	73.28

$MgHPO_4.7H_2O$ is an especially interesting salt. When freshly prepared, the crystals were exceptionally large and perfectly formed. However, in a day or two, droplets of water appeared on the walls of the glass-stoppered bottle in which the salt was stored. At the same time, the long crystals disappeared, and others appeared which proved to be the trihydrate.

It was found that the pure heptahydrate when once inoculated with the trihydrate and evacuated in the pressure-temperature apparatus formed liquid water in five minutes or less at any temperature from room temperature to at least 100°. The crystals, still in the water from which they were precipitated, left standing on the shelf changed completely into the trihydrate at the same temperature at which precipitation took place (about 22°) in about a week. It was also noticed that this change was greatly promoted by light. When the pure heptahydrate decomposed, moisture condensed only on that side of the bottle turned toward the light, and a sample of it in a glass-stoppered bottle wrapped in a black cloth required much longer to completely change into the lower hydrate than an identical unprotected sample standing beside it. It was concluded that magnesium acid phosphate heptahydrate, at least when exposed to the light, had a dissociation pressure as great as or greater than the vapor pressure of liquid water.

The Flash

It has long been known that sometimes a glow or luminesence passes through the reacting $MgNH_4PO_4.6H_2O$ while it is being ignited. There seems to be a great disagreement among authors as to the cause of this "flash," the conditions necessary for the salt to flash, and the change produced by the flash. In the table below are given a few facts observed in connection with this phenomenon.

TABLE IX

Luminescence of Magnesium Salts

Salt Used	Relative Intensity of Flash	Temperature of Flash	Nature of Product
1. $MgNH_4PO_4.6H_2O$ ppt'd cold	very strong	550-600°	Snow-white, insoluble in water, volume less than half of original.
2. $MgNH_4PO_4.6H_2O$ ppt'd at boiling temperature	strong	600-615°	Same as 1.
3. $MgNH_4PO_4.H_2O$	weak	600-625°	Snow-white, sintered, insoluble, slightly less volume than original.
4. $Mg_2P_2O_7$ by igniting $MgNH_4PO_4.6H_2O$ at 480° 8 hours	very strong	550-600°	Same as 1.
5. $Mg_2P_2O_7$ by evacuating $MgNH_4PO_4.6H_2O$ at 300° 8 hours	very strong	550-600°	Same as 1.
6. $MgHPO_4.3H_2O$	weak	550-650°	Same as 3.
7. $MgHPO_4.7H_2O$	weak	550-650°	Same as 3.

The $Mg_2P_2O_7$ (No. 5 above) was prepared by evacuating a tube built for the purpose (described under "apparatus"), in which had been placed a platinum crucible containing about 5 or 6 grams of the salt.

It was not possible to determine with sufficient accuracy the loss in weight when the small samples were ignited. However, larger samples could be successively weighed, evacuated, weighed, ignited, and weighed. Thus one sample of 5.9736 grams, after three hours evacuation at 300° weighed 2.7179 grams, and this ignited to constant weight over a Meeker burner weighed 2.7073 grams, giving a bright flash during the process. The loss in weight during the ignition was only 4 parts per 1000, and the flash was only slightly, if at all, less intensive than when $MgNH_4PO_4.6H_2O$ is used in an ordinary ignition.

For the samples ignited in the glass bulb, the loss in weight during evacuation had been from 4 to 8 parts per 1000 less than that required for the formation of pure $Mg_2P_2O_7$ prepared in a fairly large quantity and therefore in a thick layer, it was found impractical to remove the last traces of volatile matter.

In the ignitions, the results for which are recorded in tables X and XI, the average loss in weight on flashing was less than 0.2 of a milligram for a 0.1480 g. sample of pyrophosphate, or about 1.2 parts per 1000. In producing the flash the temperature of the crucible was raised from 480° to about 900°, and it seemed quite probable that the loss was in the crucible and asbestos matt rather than in the salt itself.

TABLE X

The effect of the Flash on the Weight of $Mg_2P_2O_7$

In each case the precipitate used was secured by the addition of ammonia to 45 cc. of a standard solution of $MgNH_4PO_4.6H_2O$ dissolved in very dilute hydrochloric acid.

Weight after heating one hour at 480°	Weight after 8 hours at 480°	Weight after the flash	Weight after heating 1½ hours at 925°
0.1481	0.1480	0.1478	0.1478
0.1476	0.1473	0.1471	0.1473
0.1478	0.1480	0.1478	0.1479
0.1480	0.1481	0.1478	0.1479
0.1482	0.1482	0.1480	0.1480
0.1474	0.1474	0.1474	0.1473
0.1479	0.1479	0.1478	0.1478

TABLE XI

Comparing Methods of Ignition

These precipitates were secured exactly as in Table X

(a)		(b)		(c)	
15 min. over low bunsen 1 hour over meeker	Meeker to constant weight	Dry in oven at 100°. Hottest meeker till flashed	Meeker to constant weight	1 hour at 480°. Then flash over meeker	Furnace at 900° to constant weight
0.1480	0.1476	0.1485	0.1464	0.1476	0.1474
0.1478	0.1476	0.1474	0.1475	0.1480	0.1480
0.1476	0.1475	0.1487	0.1486	0.1482	0.1482
0.1480	0.1478	0.1490	0.1489	0.1473	0.1471
0.1482	0.1483	0.1479	0.1477	0.1476	0.1475
0.1486	0.1484	0.1471	0.1470	0.1474	0.1470
0.1483	0.1482	0.1480	0.1478	0.1481	0.1480
0.1478	0.1478	0.1484	0.1483	0.1480	0.1478

Discussion of Results

The dissociation pressures obtained in this research show that magnesium ammonium phosphate hexahydrate will lose five molecules of water, when heated, at a very low temperature. The dissociation pressure of the substance is only slightly below the aqueous tension of water within the temperature interval studied, and it is equal to one atmosphere at 105° C. This explains why the monohydrate is formed when magnesium ammonium phosphate is precipitated from boiling solution, while the hexahydrate is not. The hexahydrate is stable only at lower temperatures.

The dissociation pressures also show that the monohydrate will lose both its water of hydration and it ammonia when it is heated even below 250°, where it reaches the total pressure of one atmosphere. The vapor phase at this temperature consists of approximately three-fourths water vapor and one-fourth ammonia; and equilibrium is quickly established under the prevailing conditions. Both the water vapor pressure and the ammonia vapor pressure are, therefore, great enough, and the speed of reaction is fast enough, to insure rapid dissociation when the salt is heated in an open vessel so that the gas may escape when formed. A temperature of 250° is, therefore, high enough to convert $MgNH_4PO_4.H_2O$ into $MgHPO_4$.

In the study of system 3 it was found that in the heating of $MgNH_4PO_4.H_2O$, magnesium pyrophosphate was formed whenever both water and ammonia were liberated as gases. This means that the water vapor pressure due to the loss of water of constitution by magnesium acid phosphate approached that due to the loss of water of hydration by magnesium ammonium phosphate monohydrate when both water and ammonia appear in the gaseous phase. Therefore, as soon as $MgHPO_4$ was formed it dissociated into water and $Mg_2P_2O_7$.

A summary of these facts indicates that magnesium ammonium phosphate hexahydrate loses five molecules of water at about 100°; the resulting monohydrate seems to lose one molecule of water near 200°; anhydrous magnesium ammonium phosphate has apparently lost its ammonia at about 250°; and magnesium acid phosphate its water of constitution at 250°. In other words, the highest temperature required to convert magnesium ammonium phosphate hexahydrate into magnesium pyrophosphate, according to the familiar equation,

$$2MgNH_4PO_4.6H_2O \rightarrow Mg_2P_2O_7 + 13H_2O + 2NH_3,$$

is indicated by the curve for system 3; and the transformation will go to completion at a temperature as low as 250° C.

The dissociation pressures secured seem to indicate that it is not essential to use as high a temperature for igniting $MgNH_4PO_4$ as is the general practice. Most research reports and textbooks on analytical chemistry recommend heating to 750-800° for several hours, or to 1100-1200° for an hour or more. But Miholic[10] recommends heating to 480° for two hours. His results range from 1% high to 1¼% low. But it is evident from his results and our dissociation pressure data that heating for two hours and then causing the flash would be adequate. This eliminates the possibility of a chemical reaction between the pyrophosphate and ammonia or the dissociation products of ammonia which might be entrapped.

A few ignitions, the results of which are recorded in Tables X and XI, indicate that this conclusion is probably correct. Table X shows that the flashing of the salt causes no loss in weight, a fact which shows conclusively that the flash is a change in form of magnesium pyrophosphate rather than a change of composition of the substance ignited.

A comparison of the values of (a), (b), and (c) of Table XI shows a much wider range of variation in (b). This indicates that it would not be good practice to cause the flash to occur when there is a possibility of volatile matter still unexpelled.

The statements in the literature as to the cause of the "flash" in the ignition of $MgNH_4PO_4$ are at great variance with each other. Possibly the one most commonly mentioned is exemplified by Karaoglanow and Dimitrow[13] who claim that the flash is due to the presence of organic matter. They state that the flash never occurs if all organic matter is absent; but they also state that incandescence will not occur if the salt was precipitated at boiling temperature and will if precipitated at lower temperatures. They claim that the properties of $Mg_2P_2O_7$ depend on occurrence of incandescence. Their "flashed" variety is hard, lava-like, grey to black in color, while the unflashed is amorphous, loose and quite white. Balareff[14] also obtained the two varieties, but claims that moist $MgNH_4PO_4.6H_2O$ always gives the white variety, while drying over P_2O_5 for several weeks before igniting always gives black residues. He does not believe, therefore, that the grey color resulted from impurities, and gets grey residues even when the precipitate has been filtered over asbestos. But in the same report he says that the grey salt examined through the microscope was seen to consist of white material containing black spots. Balareff[14] believes that the properties of pyrophosphate obtained depend upon the degree of hydration before ignition. Wohler[15] advances the hypothesis that luminescence is due to a type of surface fusion or sintering. Popp[16] long ago stated that the flash was likely due to an intra-molecular change within the pyrophosphate molecule.

Our results differ from most of those mentioned above. All of our samples of $Mg_2P_2O_7$, from every source, except those reported in Tables X and XI, were snow-white, and were snow-white at all stages of ignition.

Even after drying over P_2O_5 for ten weeks, white residues resulted on ignition. In the preparation of these salts contamination with filter fibers, etc. was carefully avoided. Yet, all our samples of $MgNH_4PO_4$ hexahydrate and monohydrate precipitated from either hot or cold solutions, exhibited the flash. Furthermore, $MgHPO_4.3H_2O$ and $MgHPO_4.7H_2O$ also luminesced. The only magnesium pyrophosphate which we obtained which was not white was in the case of the residues reported in Tables X and XI, some of which were light grey in color. These had been prepared in the ordinary analytical manner.

Our experiments show that the flash caused practically no loss in weight, if indeed any at all. Table X shows that the loss in weight on flashing was only 1.2 parts per 1000; and since this loss occurred when the temperature was increased from 480° to about 1000° it is very probable that the loss was in the weight of the crucible and the asbestos matt rather than in the weight of the salt itself. The luminescence in this material was still as intensive as when pure magnesium ammonium phosphate was used, which showed conclusively that the flash was due to the change from one form of $Mg_2P_2O_7$ to another.

During the flash reaction energy is liberated. The salt samples glowed brightly for an instant, and the system rose about 40°-50° when it occurred in quantities of 0.1 gram samples. The product formed must therefore contain less energy, and is, moreover, a more stable form than the original. Tests show that the more stable form is not sufficiently soluble in 0.1 molar acetic acid to give a precipitate with the zinc acetate reagent, while $Mg_2P_2O_7$ prepared by heating $MgNH_4PO_4.6H_2O$ at temperatures below 500° gives a heavy test for pyrophosphate under the same conditions. The less stable form is thus shown to be the more soluble. This is to be expected since the less stable of two solid forms of the same substance is always the more soluble.

When any of the hydrates of $MgNH_4PO_4$ and $MgHPO_4$ were converted to the pyrophosphate by heating below 500° and the residues examined through the microscope, it was found that the crystals had retained their shapes. They were, however, always opaque. During the flash this shape disappeared entirely, and only a hard, white mass remained, in which the microscope revealed no crystal forms. But it was suspected moreover that the opaque crystal-shaped particles were amorphous because they were opaque, and because the new substance would not probably have the same form as the original. Since a large amount of energy is liberated in the transformation the final amorphous-looking material was suspected of being crystalline.

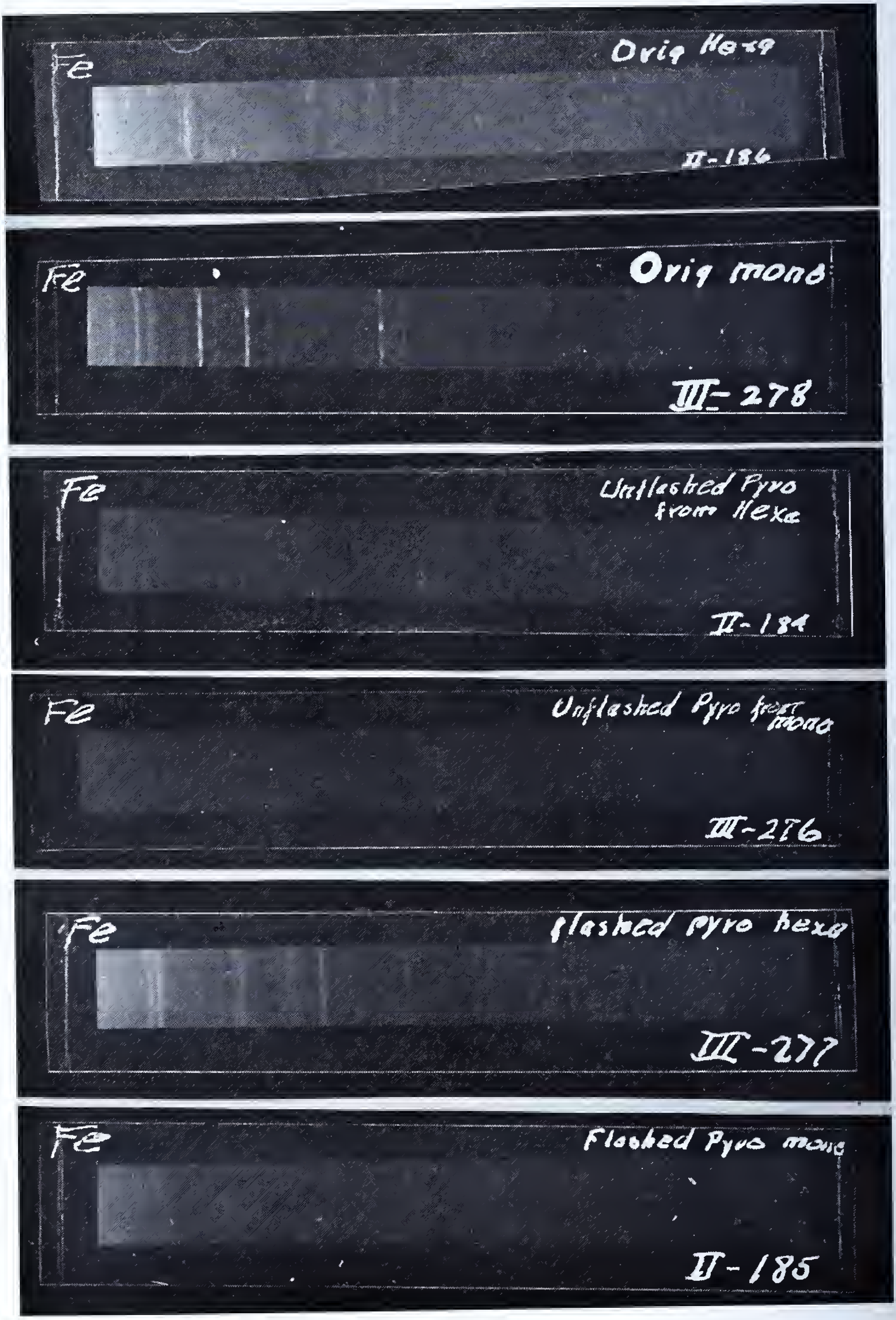

FIGURE IV.

X-ray photographs, showing different diffraction patterns for magnesium ammonium phosphate hexahydrate and magnesium ammonium phosphate monohydrate; no pattern for the unflashed pyrophosphate from either source; and the same pattern for the flashed pyrophosphate from the two sources.

In attempting to answer the questions thus raised, X-ray diffraction pattern photographs of samples of the salts in question were made. These photographs show in Figure IV very definite diffraction patterns for both magnesium ammonium phosphate hexahydrate and monohydrate; for the unflashed material from either salt no diffraction pattern whatever was found; for the flash salt from the two sources, very definite and identical patterns were found.

These X-ray diffraction patterns furnish us the final evidence that the two original salts are crystalline substances; that the unflashed pyrophosphate from both sources is amorphous; and that the two samples of flashed pyrophosphate from the two sources are crystalline and are identical.

The flash is, therefore, the sudden heating of the material to redness by the energy released in the crystallization of an amorphous substance.

Thus the crystal-shaped particles were shown to be amorphous; the amorphous-looking material was shown to be crystalline; and the flashing, which has often been called a fusion or semi-fusion has been shown to be a crystallization.

Discussion of Errors

1. By means of the silver scale and the hair-lined glass which is mounted in a steel frame and slides on a steel rod the manometer may be read to 0.2 mm. or less. Since most of the pressures read were high, the percentage errors due to this were low. For the lowest readings recorded this is about 2%, while for all readings above 20 mm. it is less than 1%.

2. The error due to levelling of the confining liquid was not more than 0.1 mm., for the two arms of the manometer are very close together, and are immediately in front of a bright, metallic mm. scale.

3. It is impossible to remove all the absorbed air from the system, and this is always an error in measuring dissociation pressures by the static method. But while this error cannot be eliminated, it is greatly reduced in this research by having a more compact outfit so that the surface of the reaction chamber is decreased by more than 50%, and by evacuating the system at least twice at an interval of twelve hours or more before a run was begun. In system 3, when the tip was broken from the bulb which contained the gas which had been generated, all but about ¼ of 1% immediately dissolved in the standard acid.

4. The error due to the vapor pressure of the mercury used as a confining liquid was eliminated by subtracting the vapor pressure of mercury from the total pressures read.

5. The errors in the measurement of temperature are very small. The e.m.f. measurements may be made with needless accuracy, and by means of a curve constructed for this particular thermocouple from the critical points of Bureau of Standards samples of metals the e.m.fs. may be very accurately converted to temperatures. The greatest errors in temperature measurement will not exceed 0.1°.

6. The error due to small changes in the temperature of the furnace is more important. The furnace-temperature can be maintained within 0.5°, which corresponds to a maximum error of about 7% in the case of $MgNH_4PO_4.6H_2O$ at the lower temperatures where 1° is the equivalent of about 7 mm. and the total pressure is about 50 mm. For the exceptionally high dissociation pressures, as of $MgNH_4PO_4.6H_2O$ at 150°, a 0.5° error will cause a pressure error of 50 mm., which, however, in a total pressure of 3400 mm. is only 1½%.

Summary

1. An apparatus is described for measuring the dissociation pressures of substances that give both water and another condensable gaseous substance.

2. A method is given for measuring and for resolving into partial pressures the dissociation pressures of salt hydrates, where both water and another gaseous substance are produced, and where the total measured pressure may be as high as 5 or 6 atmospheres.

3. The dissociation pressure for the systems:

$$\begin{aligned}
&MgNH_4PO_4.6H_2O \rightleftharpoons MgNH_4PO_4.H_2O + H_2O.\\
&MgNH_4PO_4.6H_2O \rightleftharpoons MgNH_4PO_4.H_2O + MgHPO_4.3H_2O +\\
&\qquad NH_3 + H_2O.\\
&MgNH_4PO_4.6H_2O \rightleftharpoons MgNH_4PO.H_2O + H_2O.\\
&MgNH_4PO_4.H_2O \rightleftharpoons MgNH_4PO_4 + Mg_2P_2O_7 + NH_3 + H_2O.
\end{aligned}$$

has been determined.

4. The flash in the precipitate during ignition has been studied, and an explanation given.

5. Photographs of X-ray diffraction patterns of magnesium ammonium phosphate hexahydrate and monohydrate and of amorphous and crystalline magnesium pyrophosphate are shown.

6. The use of Wood's Metal as a confining liquid is described.

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VITA

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